# U.S. GEOLOGICAL SURVEY

## POTENTIAL USE OF CLINOPTILOLITE-RICH ROCKS FOR CAPTURE AND RETENTION OF SOLUBLE LEAD IN AQUEOUS SYSTEMS SUCH AS SOILS, CONTAMINATED DRAINAGES, AND WASTE WATER

by

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#### ABSTRACT

Potassium- and calcium-rich clinoptilolite-rich rocks (CRRs) from nine deposits in western North America were tested in the laboratory to evaluate their ion-exchange affinity for dissolved lead (Pb). After Pb capture by CRRs, their ability to sequester and retain Pb during exposure to pH = 2.6 acetic acid solutions and to ammonium-rich solutions was tested. These studies were done to evaluate the potential use of CRRs for mitigation or remediation of soluble Pb pollution present in soils, drainges, and waste streams. One premise is that some K-and Ca-rich CRRs might be used for the capture of soluble Pb and retention of the ion-exchanged Pb when exposed to ammonium-rich nitrate fertilizer solutions. The objectives of this application of CRRs for Pb-pollution mitigation includes passive or semi-passive Pb capture and Pb sequestration in CRR. If retention is significant, this could substantially reduce the costs of remediation of soluble Pb pollution in soils and aqueous systems.

Side-by-side testing of the CRRs in solutions containing other cations (Na, Mg, K, Ca, and NH<sub>4</sub><sup>+</sup>) competing with Pb were done to evaluate the CRRs relative capacities and affinities for Pb. Lead-leaching tests were done after Pb loading. Up to 1.6 weight percent of Pb was exchanged into a few of the CRRs in surrogate solutions containing 47 mg/L of Pb, 75 mg/L of K, and 200 mg/L of Ca. High concentrations of Na (>10,000 mg/L) significantly depressed Pb exchange into the CRRs. Pb uptake in 10 different Pb-bearing media showed an average relative difference of 42 percent in the amount of Pb exchanged into the nine CRRs. Lead retention of CRRs varied by a relative average difference of 32 percent for eight Pb-leaching tests for which measurable Pb was lost by some of the nine CRRs tested. Some CRRs that have the highest affinity for Pb also have high Pb-retention properties in acetic acid (pH = 2.6) and NH<sub>4</sub><sup>+</sup>-rich nitrate solutions. A simple formula is given for the Pb uptake and Pb retention for comparative evaluations of the CRRs.

Some of these CRRs clearly might be useful in Pb capture and sequestration for soils and aqueous systems that contain dissolved Pb for passive mitigation of Pb pollution.

#### INTRODUCTION

Remediation of Pb pollution in soils and associated groundwaters at anthropomorphically polluted sites in the U.S. is an expensive undertaking, even though many of the Pb-polluted areas may be relatively small. Conventional soil washing or removal of soil for disposal as hazardous waste are both very expensive methods of Pb-pollution remediation. There are synthetic ion-exchange media available that are very efficient for Pb capture from aqueous solutions, but their costs are substantial, even excluding their placement and removal after Pb loading. An alternative method is a passive system where the exchange medium is placed in the soil to capture dissolved Pb as it becomes available, and the exchange medium remains in the soil. Another semi-passive system might be funnel-and-gate placement of an exchange medium amenable in suitable groundwater-flow conditions where the Pbtrapping medium could be removed after maximum Pb loading is achieved; the loaded medium could then be replaced by a fresh Pb-loading medium periodically. In this system, disposal of the Pb-loaded exchange medium may have to be treated as hazardous waste if it cannot pass the Toxicity Characteristic Leaching Procedure (TCLP) test, of the U.S. Environmental Protection Agency (1990, EPA Method 1311); if it can pass the TCLP test it might be disposed as nonhazardous waste or used as a soil amendment to enhance soil ion-exchange capacity. Synthetic zeolites with the highest Pb-exchange capacity are typically rich in exchangable Na (Hertzenberg and Sherry, 1980). Sodium is toxic to many plants when released in significant amounts. These synthetic zeolites are toxic to plants in two ways: first, when Na is released it has adverse affects on plant growth, and second, the zeolite will selectively capture the K and Ca plant nutrients from the soil after or during release of Na.

Systems of immediate Pb-pollution remediation involving either soil washing or soil removal (to a hazardous waste disposal site) may result in barren or infertile ground due to the absence of soil biota, and/or, absence of essential plant nutrients such as Mg, K, Ca, N, and P. Such aspects require critical evaluation before remediation methods are selected.

If a natural medium such as clinoptilolite-rich rocks (CRRs) that is rich in exchangable K and Ca poor in Na could be used for Pb capture and sequestration, the soil would have enhanced cation-exchange capacity with minimal release of Na. It is presumed that the most desirable Pb-pollution mitigation method(s) would retain or

restore soil fertility and leave the soil in place. The present study is an attempt to evaluate the potential use of natural K- and Ca-rich clinoptilolites for mitigation of bio-available Pb without adverse affects on plant nutrition and the associated food chain.

Potassium- and Ca-rich CRRs from nine deposits were tested in the present study. The locations of each deposit, the abbreviations used for each CRR, and the diluent minerals in each CRR are given in Appendix I. The chemical compositions for selected elements in each CRR are given in Appendix II.

#### METHODS AND RATIONALE

In this study, we examined Pb-loading capacities of the nine CRRs in the presence of common cations. We also examined the Pb-retention properties of the CRRs in dilute acetic acid (pH = 2.6) and NH<sub>4</sub><sup>+</sup>-rich nitrate solutions similar to those of liquid nitrogen fertilizers. All CRRs were tested side-by-side in solutions at rest. For the initial exposure of the CRRs to each solution, the grain size was 0.83-2.0 mm and the weights were 2.5-3.5 g. Cation competition and pH influence were evaluated using aqueous media having concentrations of 20 mg/L or much more of Mg, Na, K, Ca, and Pb. The range of pH of the exchange solutions was about 2.9 to near neutral. After CRR Pb capture from the Pb-rich solutions, the CRRs were separated from solution using filters, the CRRs were dried at 55°C, pulverized to 95% < 0.1 mm, and analyzed for Pb (and other elements) by X-ray fluorescence using a <sup>109</sup>Cd radioisotope source, a Li-drifted silicon detector, and the data reduction method of Yager and Quick (1992). Quantitative results reported for Pb are the mean of two separate analyses of each sample. Cation concentrations for solids are given as parts per million (ppm) or weight percent; cation concentrations for all liquids are given as milligrams per liter (mg/L) or weight percent.

All chemicals used for Pb-rich solutions to which the CRRs were exposed were reagent grade. These were mixed with chemically analyzed tap water that contains 1-25 mg/L each of Na, Mg, K, and Ca. This was done because all groundwaters, soil waters, or waste waters will generally have an abundance of these elements. All solutions were prepared in 16-17 L quantities. For the NH<sub>4</sub><sup>+</sup>-rich nitrate leach-test solutions, commercial fertilizer prill (NH<sub>4</sub>NO<sub>3</sub>) was mixed with tap water--as would be done for commercial preparations of liquid nitrogen fertilizer. Very high ratios of exchange liquids: CRR were used to simulate prolonged or repeated exposures of CRR to exchange liquids. Ratios of CRR to pH = 2.6 acetic acid leach solutions ranged from 1:25 to 1:30 to simulate, or exceed, the severity of the USEPA TCLP (1990, EPA Method 1311) test for Pb-loaded CRRs.

Some industrial waste waters, sewage waters, and agricultural fertilizer tail waters (runoff) may have NH<sub>4</sub><sup>+</sup> concentrations in the range of 10-200 mg/L; these concentrations are considered by some to be significant levels of NH<sub>4</sub><sup>+</sup> pollution for many environments, except when applied to soil or hydroponic environments as agricultural fertilizers. For this reason, NH<sub>4</sub><sup>+</sup> also was tested as a cation in competition with Pb. In addition, if CRRs were applied to soil for remediation of Pb pollution and left in the soil, future use of the site(s) for vegetative purposes (grass or agriculture) might involve application of NH<sub>4</sub><sup>+</sup>-bearing fertilizer(s). Therefore, NH<sub>4</sub><sup>+</sup>-rich nitrate solutions were tested as potential leachates for Pb-loaded CRRs.

#### **RESULTS**

The concentrations of Pb in each of the nine CRRs after exposure to 10 separate Pb-rich exchange solutions are given in tables that follow. The composition of each of the 10 Pb-exchange solutions, CRR grain size, solution pH, CRR dwell time in solution, and the ratio of solution volume to the weight of CRR are given in Appendix III. The composition of the Pb-leach solutions, CRR dwell time in solution, CRR grain size and ratio of leach solution volume to the weight of CRR are also given in Appendix III. In order to numerically evaluate or compare side-by side tests of the CRRs with regard to their affinity for Pb and then their retention of Pb in both dilute acetic acid solutions (pH = 2.6) and NH<sub>4</sub><sup>+</sup>-rich solutions, the following method was used to determine their relative efficiencies:

wt. percent Pb captured X 100 X [Pb remaining/Pb captured] = relative efficiency.

This relative efficiency number is converted to efficiency in percent by taking the highest relative efficiency value as 100 percent for each test and calculating the lower relative efficiency values accordingly. These numbers are given in Tables 1-10.

Table 1 shows minor Pb losses of less than 2 mg/L to 800 ml (calculated) of the 1.67 weight percent NH<sub>4</sub><sup>+</sup>

leachate solution. There were were no losses of Pb from the CRRs to the 30 ml of pH = 2.6 acetic acid solution as shown in Table 2. The losses of Pb by CRRs in the ammonium-rich solution shown in Table 3 were less than 1 mg/L of Pb. Losses of Pb from CRRs to the ammonium-rich solutions in Tables 4 and 5 were less than 4 mg/L. For the CRRs in Table 6, which captured up to 8630 ppm of Pb, losses of Pb to the ammonium-rich leachate were very significant and ranged from 3 to 8 mg/L in the leachate solution. In contrast Table 7 shows CRRs with as much as 11,700 ppm of captured Pb, but there were no Pb losses to the ammonium-rich leachate solutions. Very high concentrations of sodium (e.g. 1 wt. %) significantly suppresses the uptake of Pb by the CRRs (Table 8). The data in Table 8 shows minimal Pb losses (< 3 mg/L) from CRRs to the NH<sub>4</sub><sup>+</sup>-rich leachate. Table 9 shows the highest Pb-loading (to 16,000 ppm) into CRRs of any test done; however, when 2.5 g of the powders of each CRR were placed in 75 ml of 2.6 acetic acid for 24 h, much Pb was lost from CCO, CHI, and ZBT, whereas the other CRRs lost no Pb (Table 9). These Pb losses for the three CRRs ranged from 83 to 166 mg/L of Pb (Figure 1). This clearly demonstrates significant differences in the ability of the CRRs to sequester Pb. Table 10 shows the data for exposure of 2.35 g of these same CRRs to 628 ml of a 420 mg/L NH<sub>4</sub><sup>+</sup> leachate; only relatively small amounts of Pb (3 mg/L) were lost to the solution by some of the CRRs.

Table 1. Lead captured by CRRs in test 722, lead lost from CRRs to leachate, relative efficiency, and efficiency in percent.

CRR	Pb captured ppm	Pb lost, 1.67% NH <sub>4</sub> <sup>+</sup> leachate, ppm	Relative efficiency	Efficiency percent
cco	2450	250	22	88
CHI	2670	370	23	92
FCN	2070	70	20	80
GCM	1960	200	18	72
PBC	2190	130	20	80
PWI	2440	40	24	96
SDH	2500	0	25	100
SNM	1530	130	14	56
ZBT	1820	0	18	72

Table 2. Lead captured by CRRs in test 813, lead lost from CRRs to leachate, relative efficiency, and efficiency in percent.

CRR	Pb captured ppm	Pb lost, pH = 2.6 acetic leachate, ppm	Relative efficiency	Efficiency percent
CCO	1950	0 .	20	80
CHI	2210	<b>0</b> .	22	88
FCN	1810	0	18	72
GCM	1800	0	18	72
PBC	1900	0	19	76
PWI	2270	0	23	92
SDH	2470	0	25	100
SNM	1700	0	17	68
ZBT	2010	0	20	80

Table 3. Lead captured by CRRs in test 814, lead lost from CRRs to leachate, relative efficiency, and efficiency in percent.

CRR	Pb captured ppm	Pb lost, 1.67 $\%$ NH <sub>4</sub> <sup>+</sup> leachate, ppm	Relative efficiency	Efficiency percent
cco	3230	250	30	83
CHI	3560	0	36	100
FCN	2160	0	22	61
GCM	2260	0	23	64
PBC	2990	160	28	78
PWI	3180	0	32	89
SDH	3070	0	31	86
SNM	2310	50	23	64
ZBT	2700	90	26	72

Table 4. Lead captured by CRRs in test 817, lead lost from CRRs to leachate, relative efficiency, and efficiency in percent.

CRR	Pb captured ppm	Pb lost, 1.67 % $NH_4^+$ leachate, ppm	Relative efficiency	Efficiency percent
ССО	2600	0	26	76
CHI	2650	0	26	76
FCN	1870	0	19	56
GCM	2500	0	25	74
PBC	2310	0	23	68
PWI	2150	0	22	65
SDH	2430	0	24	70
SNM	2310	40	23	68
ZBT	3420	70	34	100

Table 5. Lead captured by CRRs in test 821, lead lost from CRRs to leachate, relative efficiency, and efficiency in percent.

CRR	Pb captured ppm	Pb lost, 1.67 % NH <sub>4</sub> <sup>+</sup> leachate, ppm	Relative F efficiency	Efficiency percent
CCO	3460	200	32	71
CHI	3200	0	32	71
FCN	3520	0	35	78
GCM	3540	80	34	76
PBC	4200	0	42	93
PWI	4060	0	41	91
SDH	3800	0	38	84
SNM	2410	140	23	51
ZBT	4860	330	45	100

Table 6. Lead captured by CRRs in test 822, lead lost from CRRs to leachate, relative efficiency, and efficiency in percent.

CRR	Pb captured ppm	Pb lost, 1.67 % $NH_4^+$ leachate, ppm	Relative efficiency	Efficiency percent
cco	5550	1700	38	54
CHI	6940	2160	48	68
FCN	5070	1070	40	57
GCM	4920	1500	34	48
PBC	5170	1140	40	57
PWI	8630	2480	61	87
SDH	8300	1300	70	100
SNM	4300	1000	33	47
ZBT	4830	1510	33	47

Table 7. Lead captured by CRRs in test 909, lead lost from CRRs to leachate, relative efficiency, and efficiency in percent.

CRR	Pb captured ppm	Pb lost, 1.67 % NH <sub>4</sub> <sup>+</sup> and acetic (pH = 2.6) leachates, ppm		Efficiency percent
CCO	9200	0	92	79
CHI	11700	. 0	117	100
FCN	8500	0	85	73
GCM	9100	0	91	78
PBC	8600	0	86	74
PWI	11000	0	110	94
SDH	10500	0	105	90
SNM	5700	0	57	49
ZBT	7300	0	73	62

Table 8. Lead captured by CRRs in test 920, lead lost from CRRs to leachate, relative efficiency, and efficiency in percent.

CRR	Pb captured ppm	Pb lost, 1.67 % NH <sub>4</sub> <sup>+</sup> leachate, ppm	Relative efficiency	Efficiency percent
CCO	1160	140	10	71
CHI	1360	70	13	93
FCN	1010	0	10	71
GCM	880	0	9	64
PBC	1380	0	14	100
PWI	900	0	9	64
SDH	1330	0	13	93
SNM	790	0	8	57
ZBT	1270	270	10	71

Table 9. Lead captured by CRRs in test 1003, lead lost from CRRs to pH = 2.6 acetic acid solution, relative efficiency, and efficiency in percent.

ppm	acetic leachate, ppm	efficiency	y percent
12000	1000	110	69
14000	1000	130	81
10000	0	100	62
11000	0	110	69
12000	0	120	75
16000	0	160	100
16000	0	160	100
8400	0	84	52
10000	. 2000	80	50
	14000 10000 11000 12000 16000 8400	14000     1000       10000     0       11000     0       12000     0       16000     0       8400     0	14000     1000     130       10000     0     100       11000     0     110       12000     0     120       16000     0     160       16000     0     84

**Table 10.** Lead remaining in CRRs of 1003 test after pH = 2.6 acetic acid leach in Table 9, and lead lost in  $NH_4^+$  = 420 mg/L leachate, relative efficiency, and efficiency in percent.

CRR	Pb remaining after acetic leach, ppm	Pb lost to 420 mg/L $\mathrm{NH_4}^+$ leachate, ppm	Relative efficiency	Efficiency percent
cco	11000	520	105	66
CHI	13000	0	130	81
FCN	10000	480	95	59
GCM	11000	400	106	66
PBC	12000	300	117	73
PWI	16000	800	152	95
SDH	16000	0	160	100
SNM	8400	550	78	49
ZBT	8000	860	71	44

The leaching tests using dilute acetic acid (pH = 2.6) were done to expose the Pb-exchanged CRRs to conditions more stringent than the Toxicity Characteristic Leaching Procedure of the U.S. Environmental Protection Agency (1990, EPA Method 1311). For Method 1311 the material to be tested must pass through a 9.5 mm sieve; it is then exposed to an acetic acid extraction liquid (pH = 2.88) that is 20 times the weight of the solid phase in a zero-headspace vessel that is rotated in an end-over-end fashion at 30 rpm for 18 hours (1990, EPA Method 1311). The 0.7-micron-filtered extraction liquid is then quantitatively analyzed. If the amount of Pb in the extraction fluid exceeds 5 mg/L, the material tested is considered toxic or hazardous.

The exposure of Pb-loaded CRRs to NH<sub>4</sub><sup>+</sup>-rich solutions was done to evalute the potential of leaving CRR in the soil after uptake of Pb by cation exchange. In agricultral fertilizer practices for high-value crops, cropseason synthetic N-fertilizer applications may be as much as 400 pounds of N per acre where the soil is N deficient. If NH<sub>4</sub>NO<sub>3</sub> (36 % N) prill (beads) is used, it is generally broadcast evenly on the surface and then mechanically

worked into the soil to depths of 6-9 inches. This produces NH<sub>4</sub><sup>+</sup> concentrations in the soil as follows:

NH <sub>4</sub> +, ppm	Soil tilled depth, inches
72	9
96	6
192	3

For row crops of high value (e.g. lettuce, potatoes, and sugar beets) and grown with a synthetic NH<sub>4</sub>NO<sub>3</sub> fertilizer, a solution called AN 20 (57.1 % NH<sub>4</sub>NO<sub>3</sub> and 42.9 % water) is placed by "banding" or "knifing" the liquid (injection into the soil below the roots) of the row crop. Such applications are generally done at a maximum of 50 pounds of N per acre several times during the growing season. For row crops 30 inches apart, banding with liquid AN 20 in a 3-inch width produces NH<sub>4</sub><sup>+</sup> concentrations in the soil as follows:

NH <sub>4</sub> +, ppm	Soil tilled depth, inches
120	9
160	6
320	3

These NH<sub>4</sub><sup>+</sup>-soil concentrations for synthetic N fertilizers are given to show that under agricultural and horticultural conditions, relatively high NH<sub>4</sub><sup>+</sup> concentrations could displace Pb present in high concentrations for <u>some</u> CRRs. It is for this reason that such high ratios of NH<sub>4</sub><sup>+</sup>-leach solutions to CRRs were used (Appendix III). In addition, the concentrations of NH<sub>4</sub><sup>+</sup> in the leach solutions exceeds those of ammonium nitrate fertilizer applications given above by a factor of 1.3 to 52 times.

#### **SUMMARY**

Table 11 gives the mean of the efficiency percentages of each CRR for each of the ten tests presented in Tables 1-10. The means for each CRR for the ten tests were then normalized so that the highest mean of the CRRs was taken as 100 percent and the lower means then calculated on this basis (Table 11). These normalized mean efficiencies are shown on Figure 2.

Table 11. Mean of efficiency percentages for each CRR for 10 tests presented in Tables 1 through 10. Normalized means are given last.

CRR	CCO	CHI	FCN	GCM	PBC	PWI	SDH	SNM	ZBT
Mean of 10 tests	74	85	67	68	77	87	92	56	70
Normalized Mean	80	92	73	74	84	94	100	61	76

Data presented here are interpreted to indicate that some of these K- and Ca-rich clinoptilolite-rich rocks (CRRs) have potential for use in mitigation of Pb pollution in soils and Pb-contaminated water. Their abilities to capture and sequester Pb varies widely, and it appears that some are nearly twice as efficient as others. It is clear that their use in these applications should be tested on a site-specific basis.

Zamzow and others (1989) have done the most extensive studies of Pb uptake by zeolitic rocks, including the influence of competing cations. Leppert (1990) gave data showing that CRR mixed with Pb-contaminated soil could capture significant amounts of Pb. However, the high amounts of Pb (2.2 wt. %) in the soil after treatment overwelmed any beneficial effect the zeolite had and the plants died.

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#### APPENDIX I

Locality data, abbreviations, and diluent minerals in clinoptilolite-rich rocks used in the present study. Minerals determined by X-ray diffraction by G.A. Desborough and Richard Sheppard (U.S. Geological Survey). [Minerals listed in decreasing order of abundance; "clay" refers to layer silicates with a 10 Å spacing; tr. = trace]

Locality and abbreviation

Diluent minerals

British Columbia

Princeton-PBC

Opal, feldspar, mordenite, quartz

(tr.)

Colorado

Creede-CCO

Opal, K-feldspar, plagioclase,

quartz, clay

Idaho

Crisman Hill-CHI

Opal, K-feldspar

Preston-PWI

Opal

Montana

Grasshopper Creek-GCM Opal, K-feldspar, plagioclase

Nevada

Fish Creek-FCN

K-feldspar, quartz, plagioclase

New Mexico

Winston-SNM

Opal, clay (tr.)

South Dakota

Rocky Ford-SDH

Plagioclase, calcite, quartz, opal, K-feldspar, clay (tr.)

<u>Texas</u>

Tilden-ZBT

Opal, clay, calcite

APPENDIX II

Chemical composition of selected elements in raw clinoptiloliterich rocks (CRRs) determined by X-ray fluorescence analysis. (Analyst: G.A. Desborough)

CRR	K	Ca	Fe	Cu	Zn	Rb	Sr	Zr	Ва	Pb
	weig	ht pe	rcent			-parts				
cco	3.6	1.8	0.9	<20	50	200	580	140	650	50
CHI	4.2	0.9	1.5	30	120	200	150	540	1600	<30
FCN	3.4	1.6	0.6	<20	60 <sup>-</sup>	190	300	180	670	35
GCM	2.8	1.9	0.5	20	55	95	530	55	1480	<30
PBC	2.1	1.6	1.8	25	125	50	490	320	2000	<30
PWI	3.6	1.7	1.1	<20	55	160	120	350	1100	<30
SDH	4.0	1.7	1.4	20	60	90	460	170	. 700	35
SNM	2.0	2.7	0.9	30	70	70	1700	190	1000	40
ZBT	1.2	3.1	0.8	<20	45	50	500	160	800	<30

#### APPENDIX III

Conditions and concentrations of exchange solutions used in this study of Pb uptake by clinoptilolite-rich rocks (CRR) and the extractability of Pb from CRRs in acetic acid and  $\mathrm{NH_4}^+$ -rich leach solutions.

[CRR grain size; crs = 0.8-2.0 mm, fn = 95% < 0.1 mm; Ratio of Solution/CRR = Solution volume./CRR weight

Test	ъĦ	time	CDD	Na	Mg	K	Ca	Pb	NH <sub>4</sub> +	Ratio of
1636	PII		grain	110	_				14114	Solution/
		111.	size		mg/L, or %					CRR
			2176							CRR
722	4.6	24	crs	<20	<20	100	270	47	<1	267
Leach			fn	<20	<20	<25		<0.01	1.67%	267
813	3.7		crs	<20	<20	75	200	47	57	267
Leach			fn			etic a	cids	solution		25
814	3.0	43	crs	<20	<20	75	200	47	57	267
Leach			fn	<20	<20	<25	<25	<0.01	1.67%	267
817	3.0	24	crs	<20	<20	<25	<25	47	171	267
Leach	6.0	24	fn	<20	<20	<25	<25	<0.01	1.67%	267
821	2.9	24	crs	<20	<20	<25	<25	47	<1	267
Leach	5.9	24	fn	<20	<20	<25	<25	<0.01	1.67%	267
822	3.8	25	fn	<20	<20	75	200	47	57	267
Leach	5.8	24	fn	<20	<20	<25	<25	<0.01	1.67%	267
909	4.3	24	crs	<20	<20	75	200	47	<1	267
	4.3	24	crs	<20	<20	75	200	47	<1	267
	4.3	24	crs	<20	<20	75	200	47	<b>&lt;</b> 1	267
	4.3	24	crs	<20	<20	75	200	47	<1	267
Leach	6.0	24	fn	<20	<20	<25	<25	<0.01	1.67%	267
Leach	2.6	24	fn	dil	ute ace	etic a	cid s	solution	l	30
920	6.4	24	crs	1.06%	1290	380	400	47	<1	267
Leach	5.9	24	fn	<20	<20	<25	<25	<0.01	1.67%	267
1003	4.1	. 24	crs	<20	<20	75	200	47	<1	267
	4.1	24	crs	<20	<20	75	200	47	<1	267
	4.1	24	crs	<20	<20	75	200	47	<1	267
Leach	2.6	24	fn	dil	ite ace	etic a	cid s	solution	L	30
Leach	6.7	24	fn	<20	<20	<25	<25	<0.01	420	267

#### APPENDIX IV

Reagents used for preparation of Pb-bearing solutions exclusive of synthetic sea water.

Calcium chloride-CaCl<sub>2</sub> Potassium acetate-KC<sub>2</sub>H<sub>3</sub>O<sub>2</sub> Lead nitrate-Pb(NO<sub>3</sub>)<sub>2</sub> Ammonium nitrate-NH<sub>4</sub>NO<sub>3</sub>

Reagents used for preparation of Pb-bearing synthetic sea water

Test 920 Appendix III

Calcium chloride-CaCl<sub>2</sub>
Magnesium chloride-MgCl<sub>2</sub>
Potassium chloride-KCl
Sodium chloride-NaCl
Sodium sulfate-Na<sub>2</sub>SO<sub>4</sub>.10H<sub>2</sub>O
Lead nitrate-Pb(NO<sub>3</sub>)<sub>2</sub>

### Pb lost by CRRs 1003 test in acetic pH = 2.6 soln at 1:30 ratio (CRR:solution)

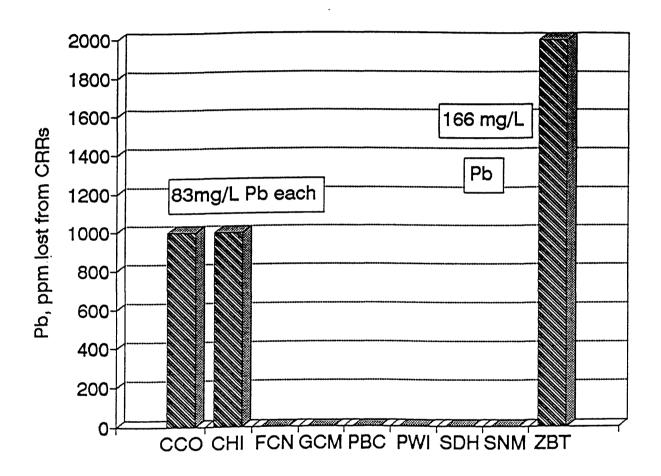


Figure 1. Bar graph showing the amounts of Pb lost from 1003 test of clinoptilolite-rich rocks (CRRs) when exposed to acetic acid solutions of pH = 2.6 in a ratio of 1 g CRR: 30 ml solution for 24 hours. The amounts of Pb lost to the solutions are also given. (Abbreviations for CRRs are given in Appendix I.)

## Normalized mean of 10 CRR tests of efficiency of Pb capture and retention

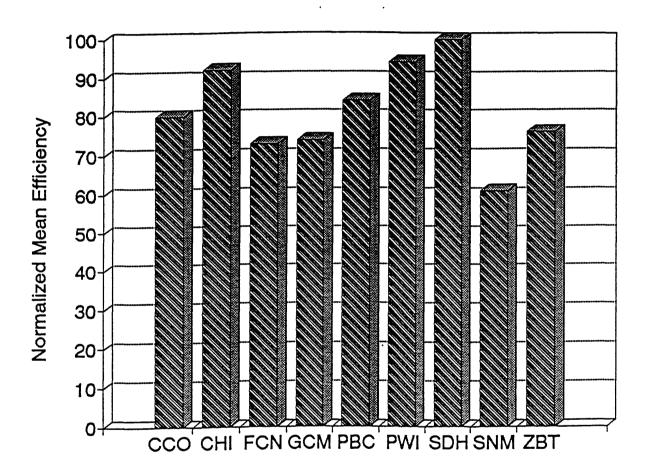


Figure 2. Graph showing the normalized mean of 10 calculated efficiencies of clinoptilolite-rich rocks to capture and sequester Pb during exposure to pH = 2.6 acetic acid solutions and  $\mathrm{NH_4}^+$ -rich solutions. (Abbreviations are given in Appendix I).